

Fundamental Studies of Nanocrystalline Si and Ge for PV

Vikram L. Dalal
Iowa State University

Introduction

- Growth chemistry of nc Si:H and Ge:H
- Why do some materials have $\langle 111 \rangle$ grain and some $\langle 220 \rangle$?
- What controls grain size? How do we get larger grains?
- What are the mobilities in device-type structures?
- What are the diffusion lengths of minority carriers?

Why growth chemistry?

- Typical nc-Si:H has small grains, 10-15 nm
- Idea is to understand how to get large grains while preserving good properties such as grain-boundary passivation
- We know high T's will get large grains-but break Si-H bonds - increase recombination
- Have to understand growth chemistry - how do grains grow - what limits them

Influence of grain size

- Larger the grain size, large the mobility should be.
- As grain size increases, everything else remaining the same, GB recombination decreases
- Higher mobility and lower recombination lead to longer minority carrier diffusion lengths - hence better PV properties

Growth

- 2 different techniques will be used
- VHF plasma and REMOTE hot wire
- Look at structural and electronic properties
- Structure: x ray (detailed) and Raman spectrum
- Look at both nc-Si and nc-Ge
- Electronic: Defects and diffusion lengths

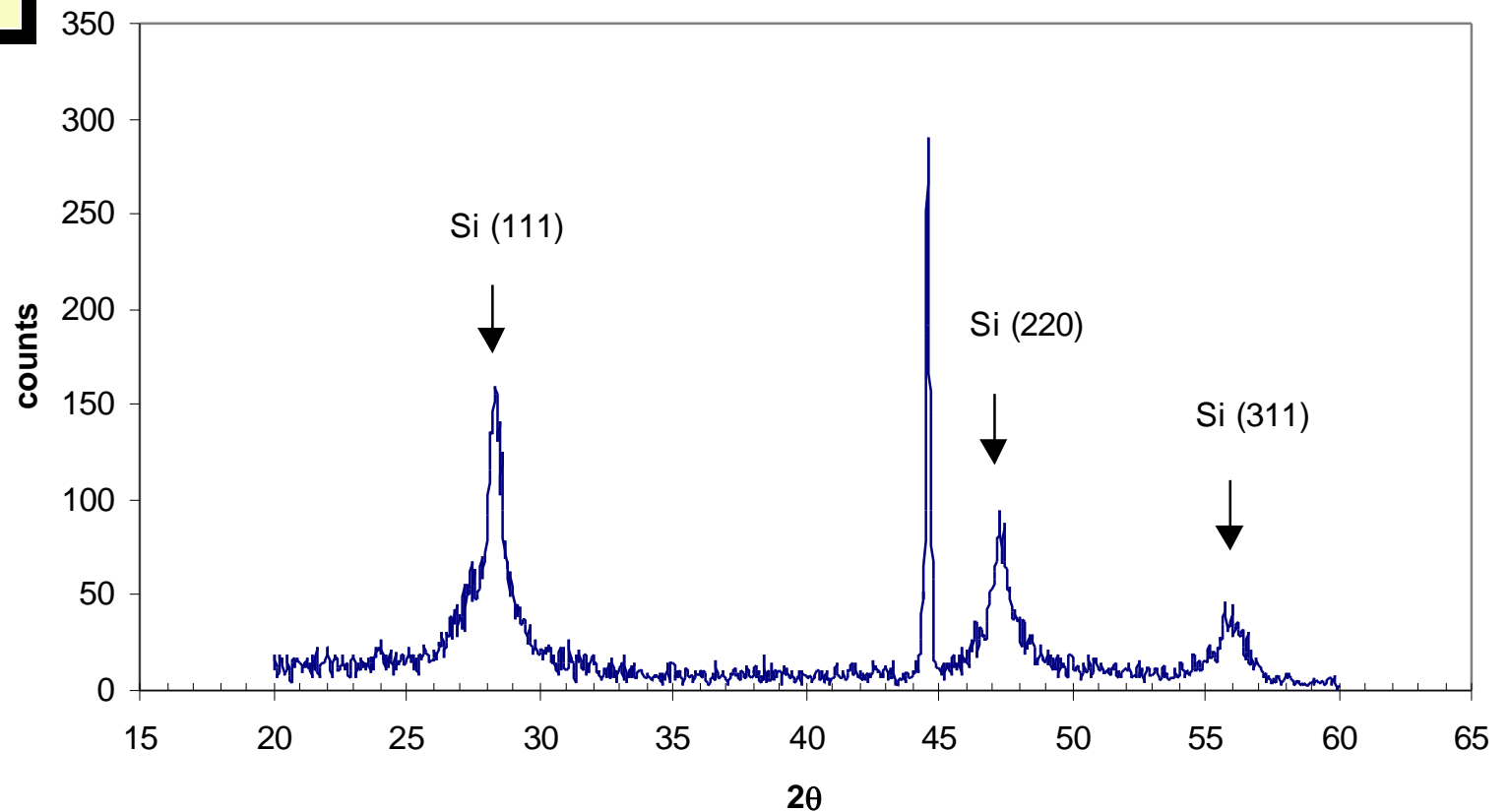
VHF growth

- Standard parallel plate geometry
- LOW pressure regimes (25 mTorr to 500 mTorr)
- silane + hydrogen - different ratios
- Growth temperatures of ~300 C

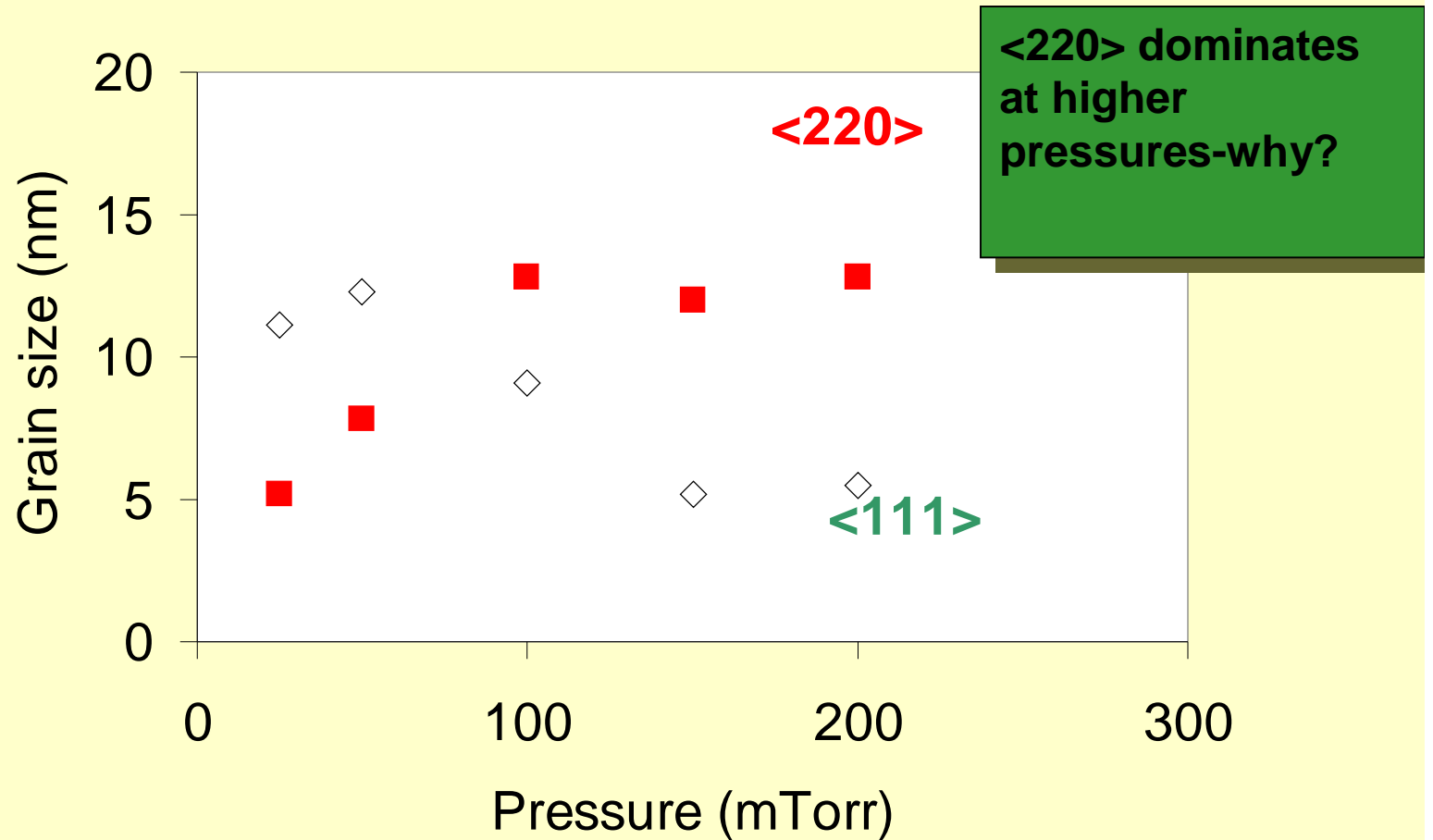
VHF Si-X-ray diffraction(ss substrate)

Both $\langle 111 \rangle$ and $\langle 220 \rangle$

XRD 1-4532

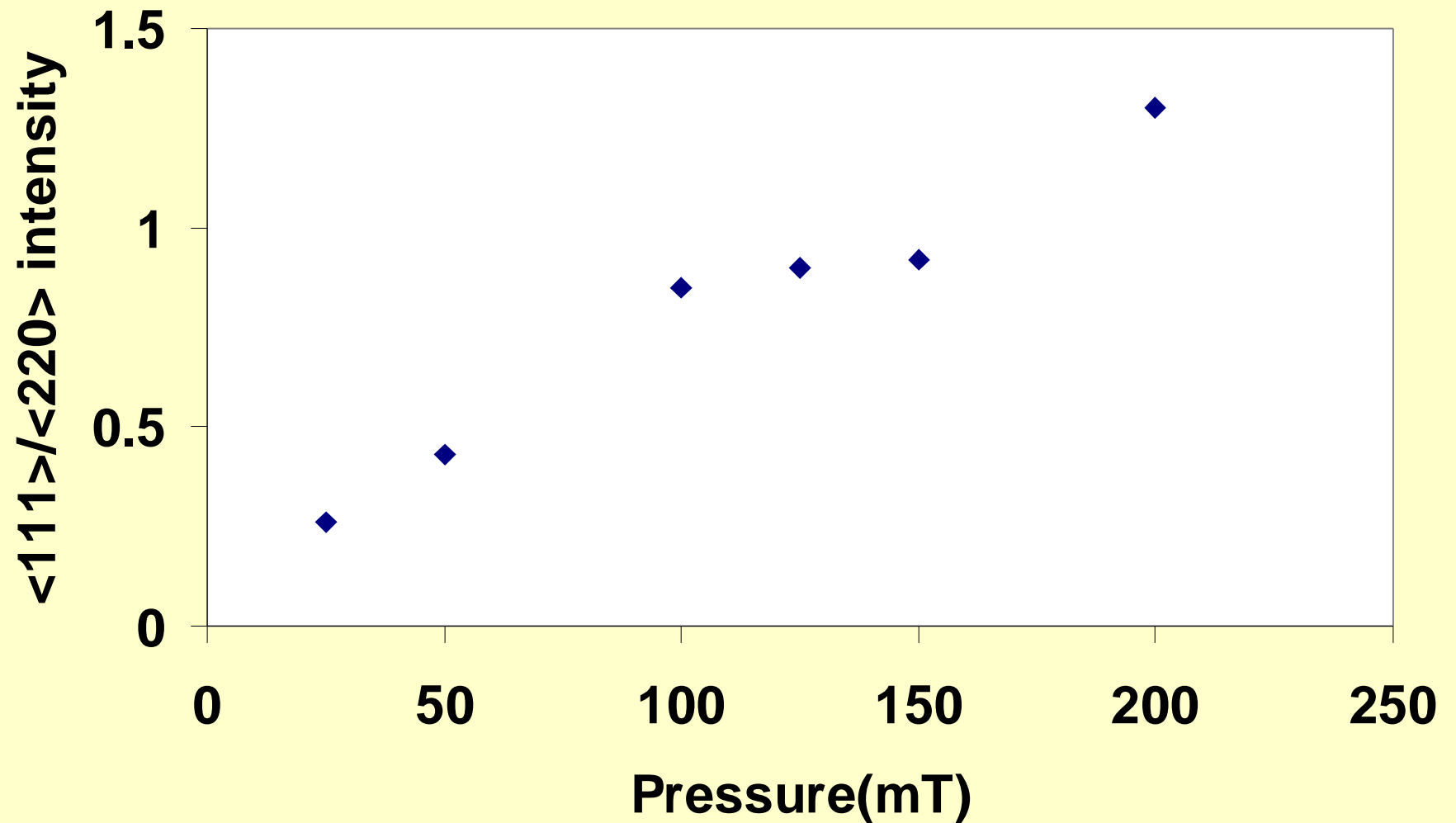


Influence of pressure on grain size



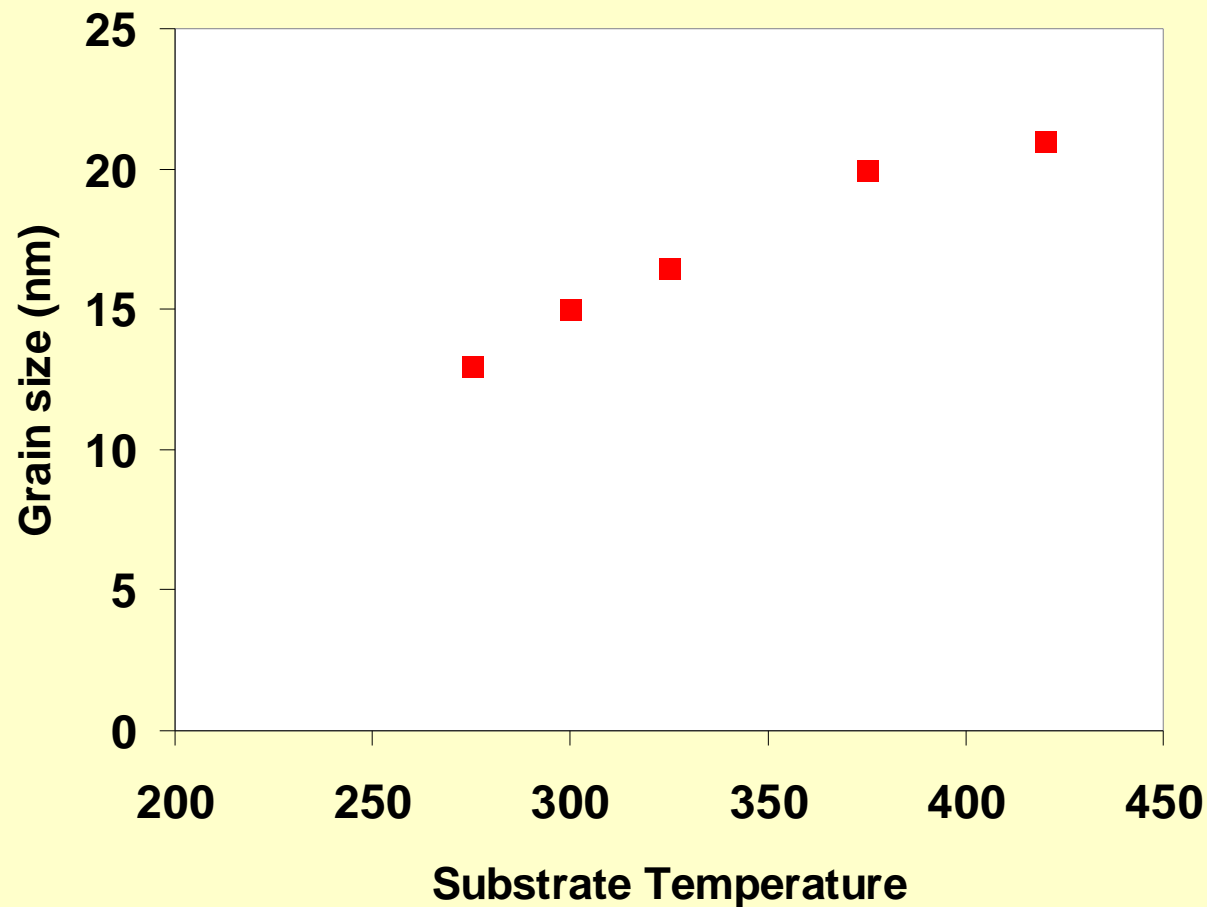
Ratio of $\langle 111 \rangle / \langle 220 \rangle$ peaks

VHF films



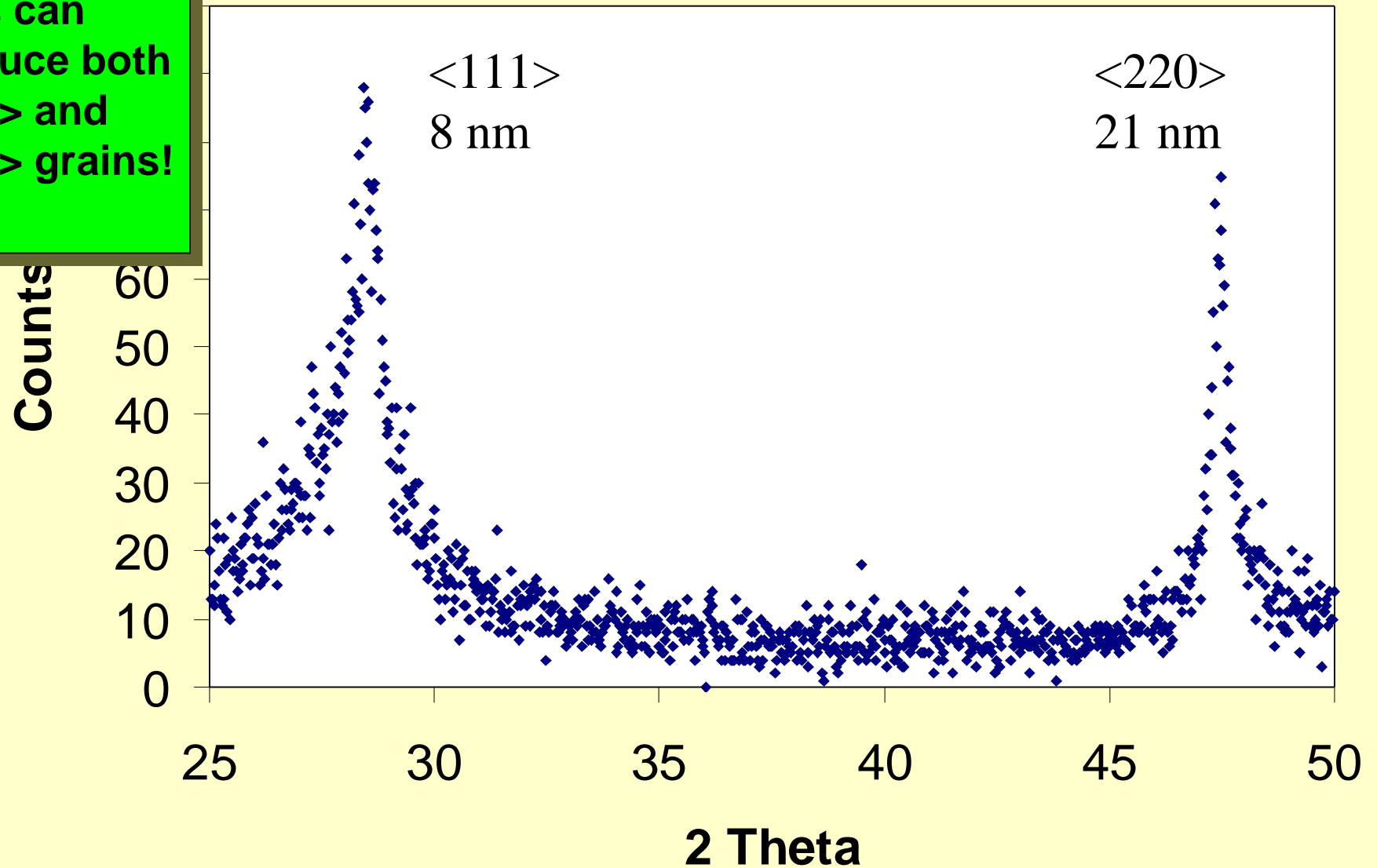
Grain size vs temperature-nc

Si, VHF, 50 mTorr

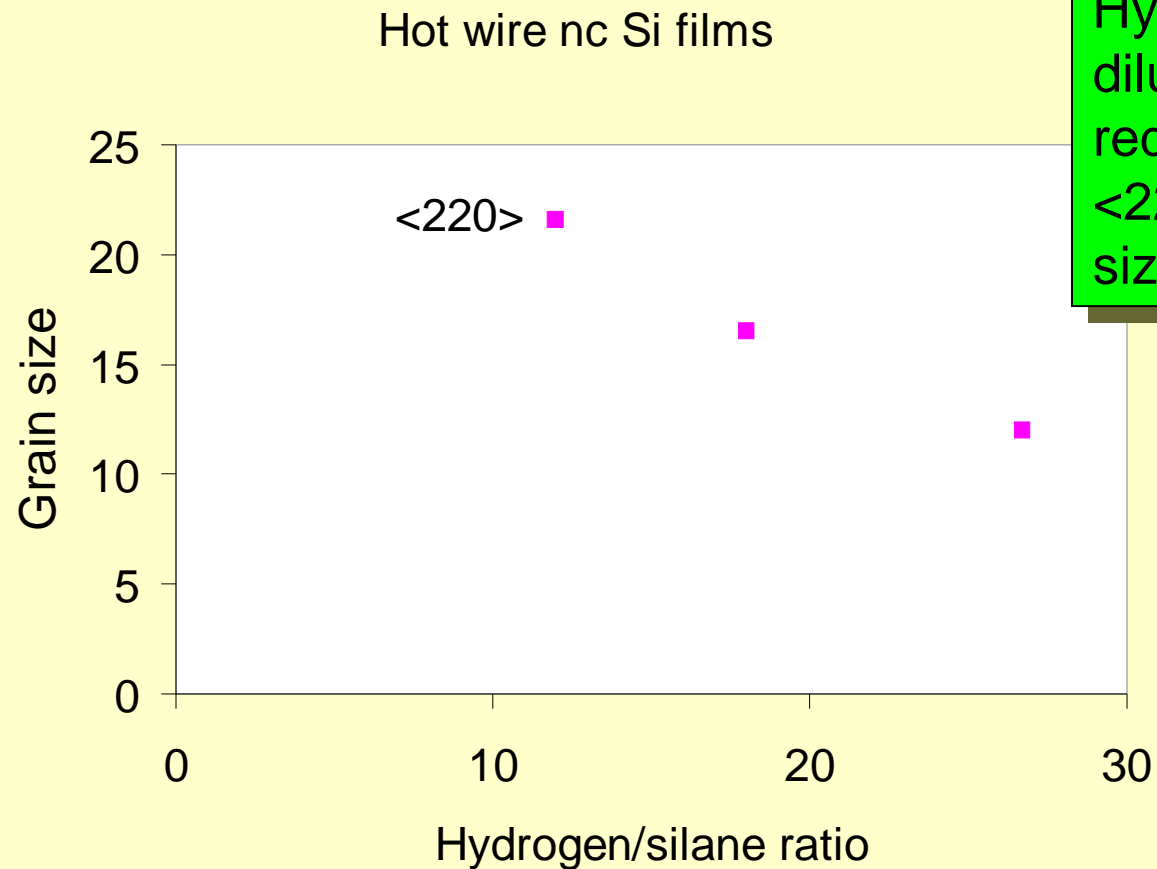


X-ray spectrum of hot wire nc-Si films

Hot wire films can produce both $\langle 111 \rangle$ and $\langle 220 \rangle$ grains!



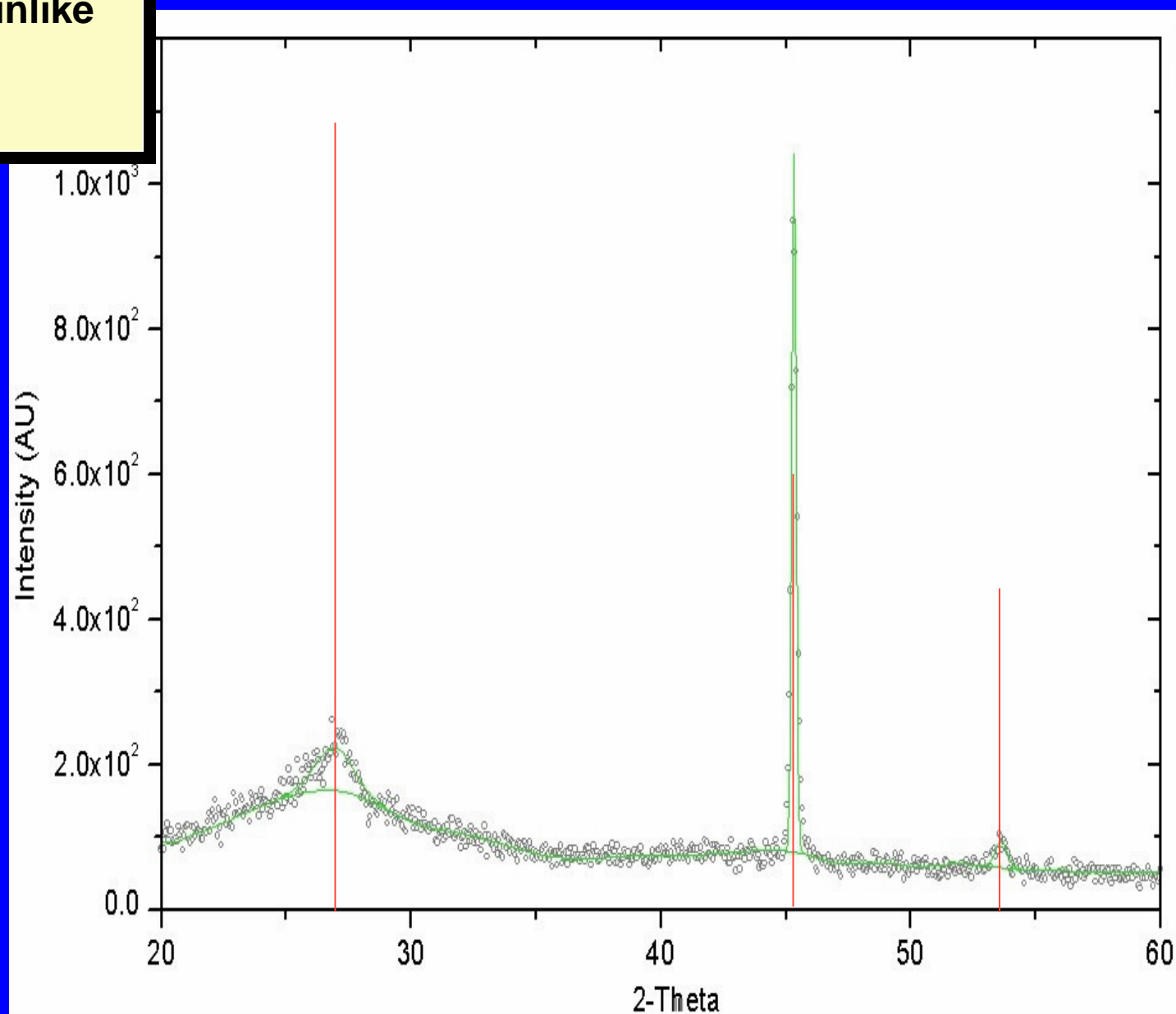
Remote Hot wire films, grain size vs hydrogen dilution



Increasing
Hydrogen
dilution
reduces
<220> grain
size

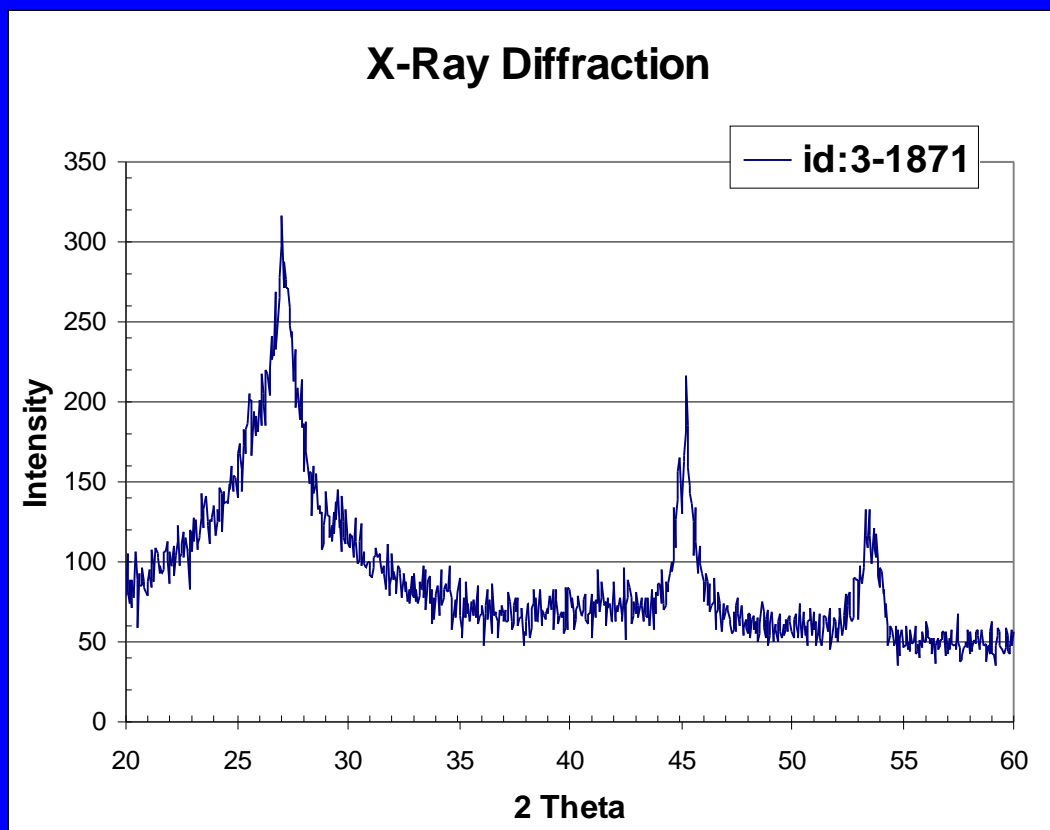
Primary
orientation
<220>- unlike
nc-Si

X-ray spectrum of nc Ge:H, 250 C growth, ECR



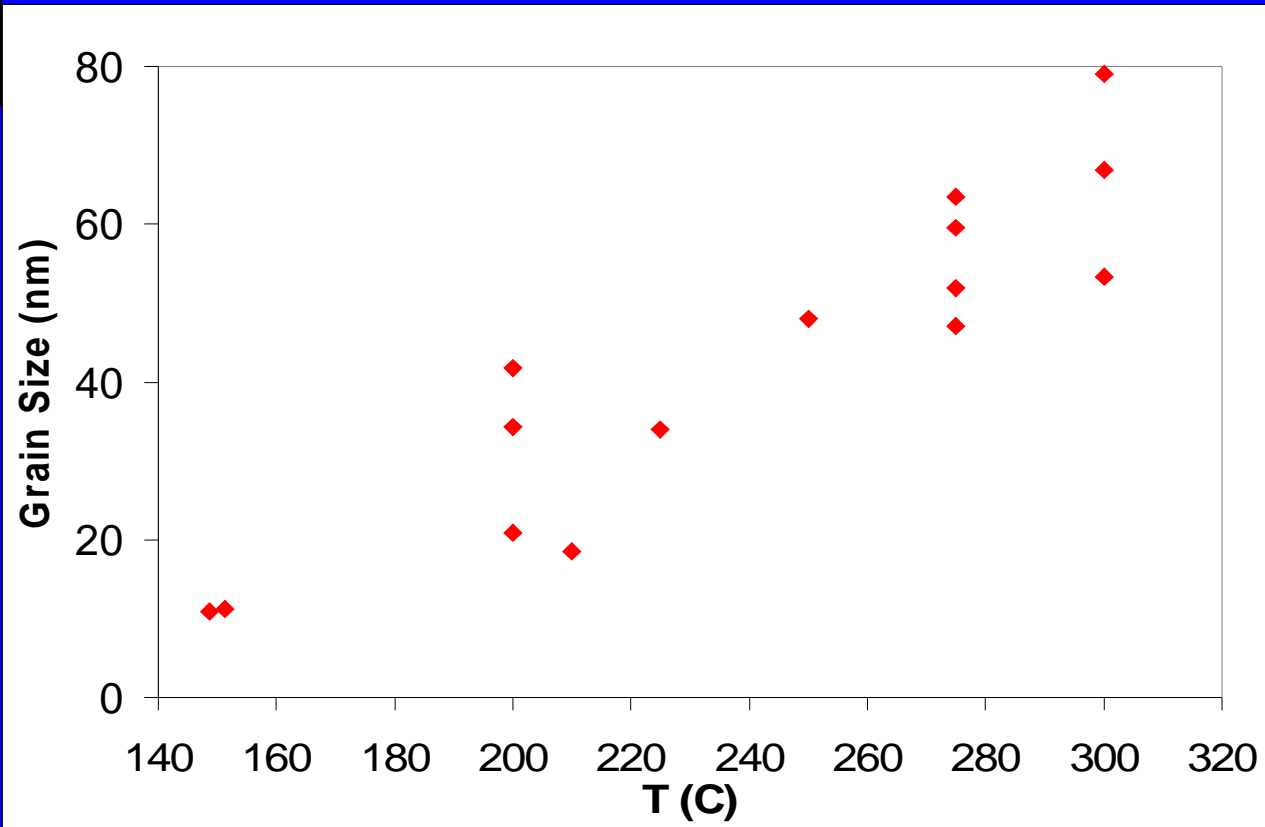
At low T
(130C),
multiple
orientations

Low Temp nc-Ge:H



Grain size
increases with
growth
temperature

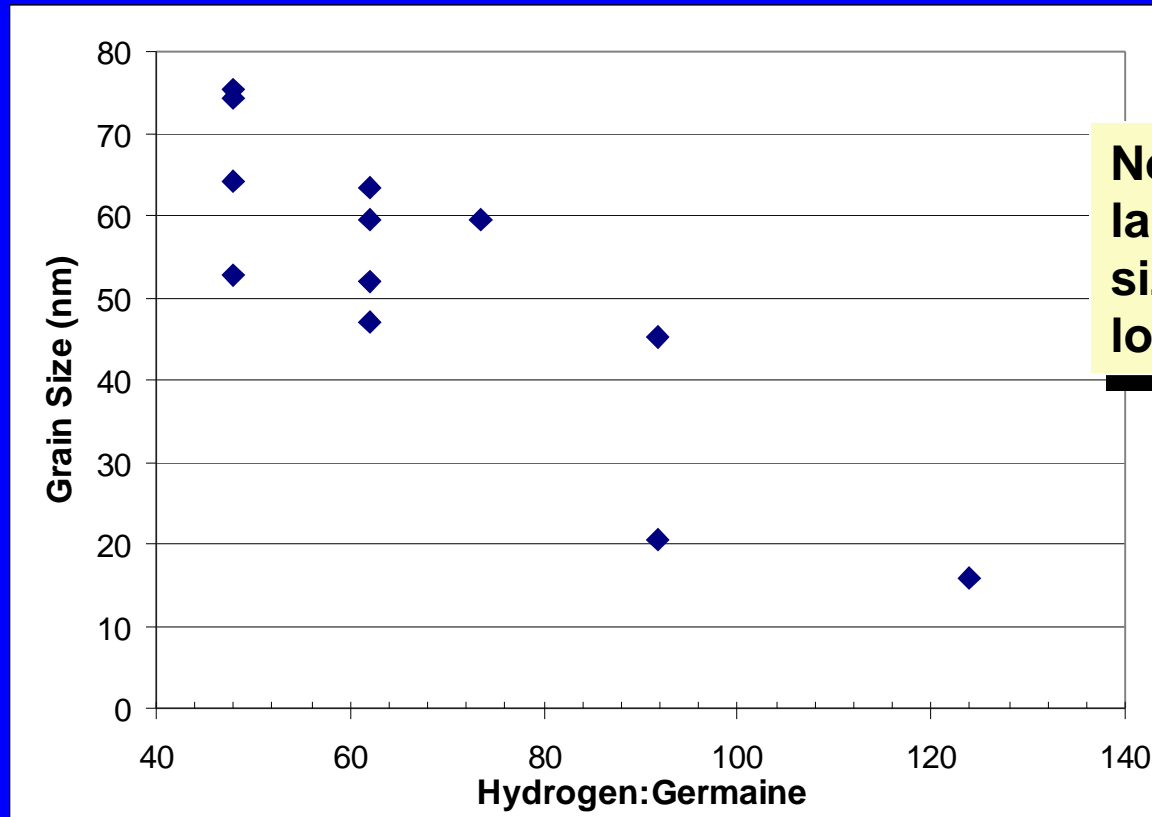
GE: Grain Size - Temperature



- Surface diffusion
- Removal of H bonding at GB at higher T
- Similar to nc-Si data

Increasing H
dilution
reduces grain
size

Ge: <220> Grain Size - H Dilution



Note the very
large grain
size - 75 nm at
lower dilutions

- H etching
- H passivation of GB lowers γ – driving force
- More nucleation sites

What is going on?

- For both Si and Ge, higher T's lead to larger $\langle 220 \rangle$ grains
- $\langle 220 \rangle$ grain size DECREASES as H dilution increases , or pressure decreases
- At a give temperature (250 C) Ge grains much larger than Si
- Ge predominantly $\langle 220 \rangle$ at normal growth temperatures, but at lower T's, both $\langle 111 \rangle$ and $\langle 220 \rangle$

Too much H
may be bad!

Why?

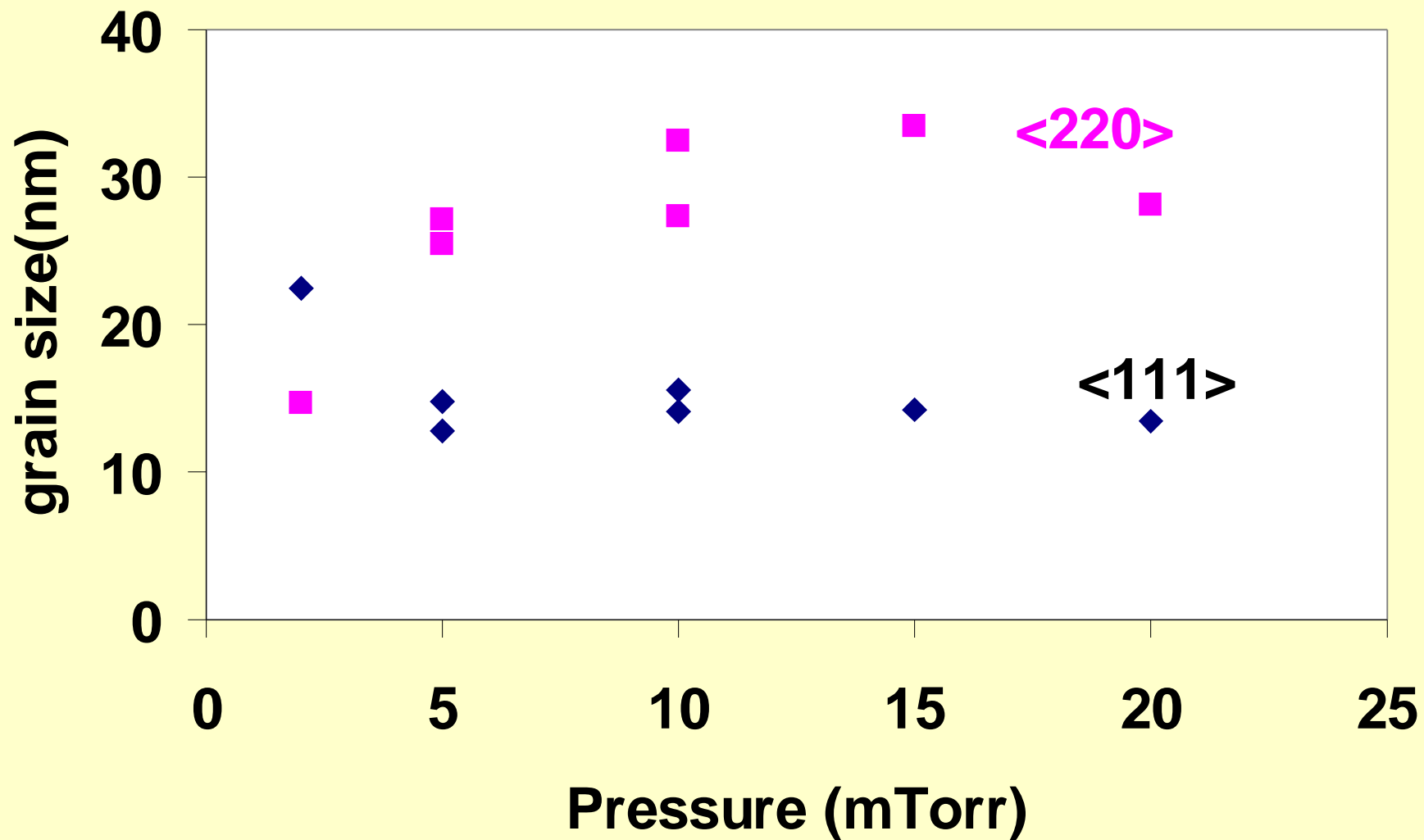
- The natural growth direction is $\langle 220 \rangle$, because of larger surface energy for (110) vs (111) planes
- Surface energy of (110) plane in Si is 2 J/m^2 and that of (111) plane is 1.45 J/m^2
- Bonded H interferes with growth of $\langle 220 \rangle$ grains - in Ge, at a given temperature, less bonded H, therefore larger grains
- As temp. decreases, more bonded H, smaller grains
- Excess H radicals or ions may lead to random nucleation, both $\langle 111 \rangle$ And $\langle 220 \rangle$

Can we get large grains in Si at normal (~ 300 C) temperatures?

YES, by controlling pressures in remote hot wire

Remote hot wire means filament does not heat up the substrate - 11.5 cm distance

hot wire nc Si



Conclusions on Growth

- We can get larger grain sizes by carefully controlling growth conditions
- $\langle 220 \rangle$ is the natural growth direction, and $\langle 111 \rangle$ is due to random nucleation
- More work needed to get larger grains

New Method for measuring Mobility in device type structures

- Most films as-grown are n type
- Hall effect gives lateral mobility - we need mobility along the growth direction
- Hall measurements generally on films on glass - devices are on a conducting substrate- maybe different materials
- Two methods: Time of flight (Eric Schiff) and Space charge limited currents (Dalal)

SCLC

- Under space charge, $J = 1.1 \epsilon \mu V^2/L^3$
- Set up SCLC conditions - Field $> qN_t L/\epsilon$
- If traps are $\sim 1E14/cm^3$ range, for 1 micrometer thickness, $V > .16 V$, and for $1E15$, $1.6 V$
- Measure J vs V^2 - verify V^2 behavior - only unknown is mobility

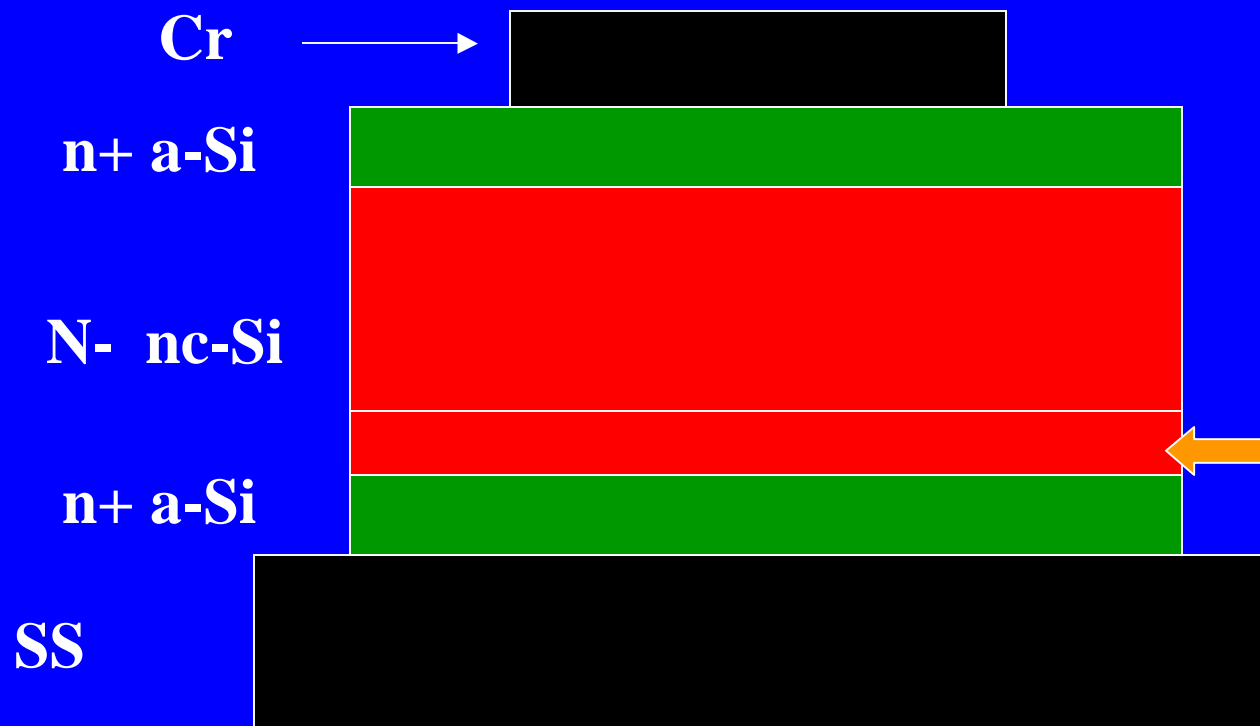
Experimental problems

- Got to make sure there is little a-Si layer - otherwise effective mobility will be low - high resistance region will dominate low resistance region
- Must get rapid nucleation on n+ substrate

Current data
on hot wire
grown nc-Si-
will measure
VHF grown
materials later

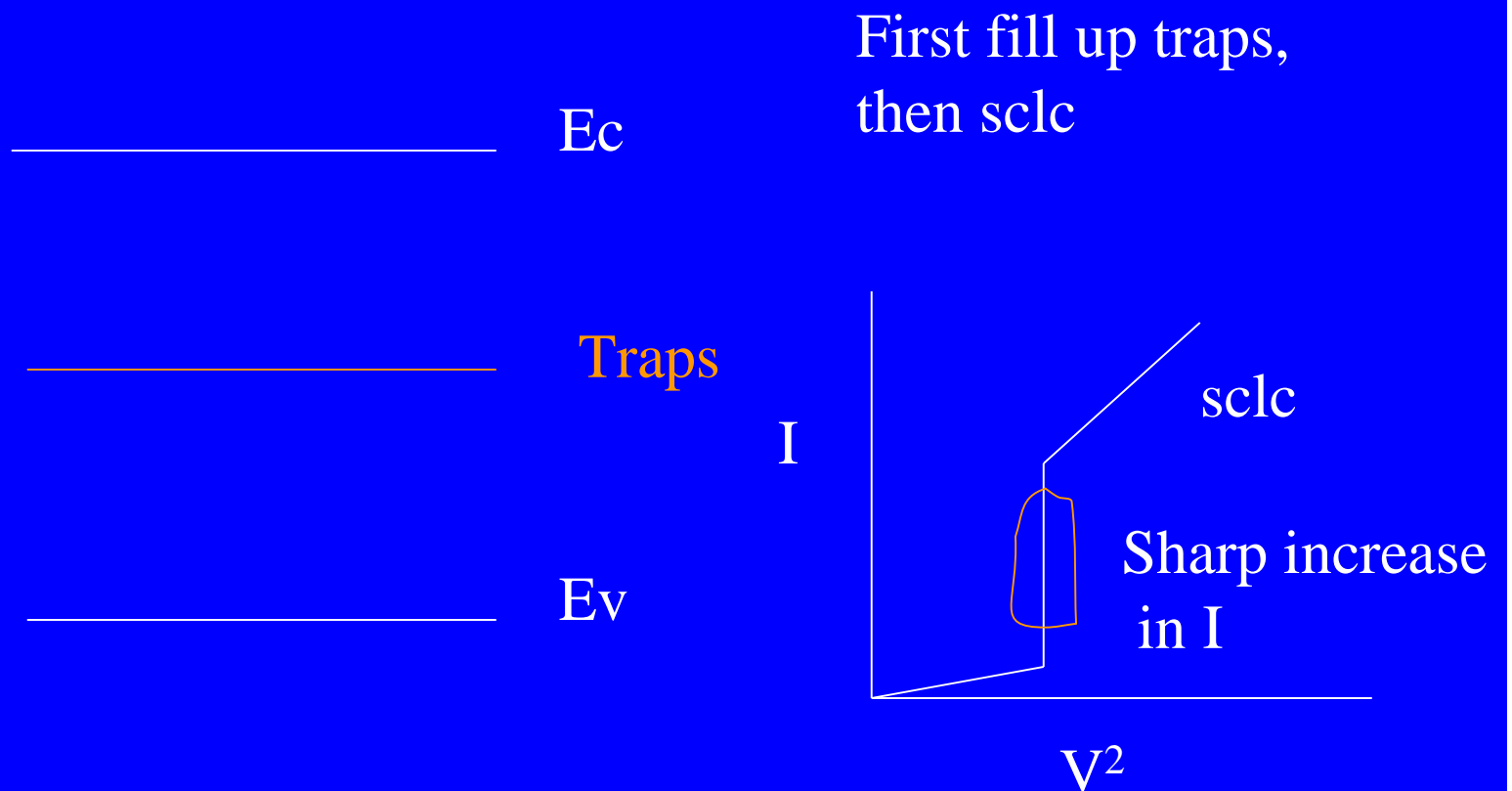
SCLC structure

This structure will not
work for holes - must
use nanocrystalline p
type injectors for
holes - reason : band
offsets between a-Si
and c-Si

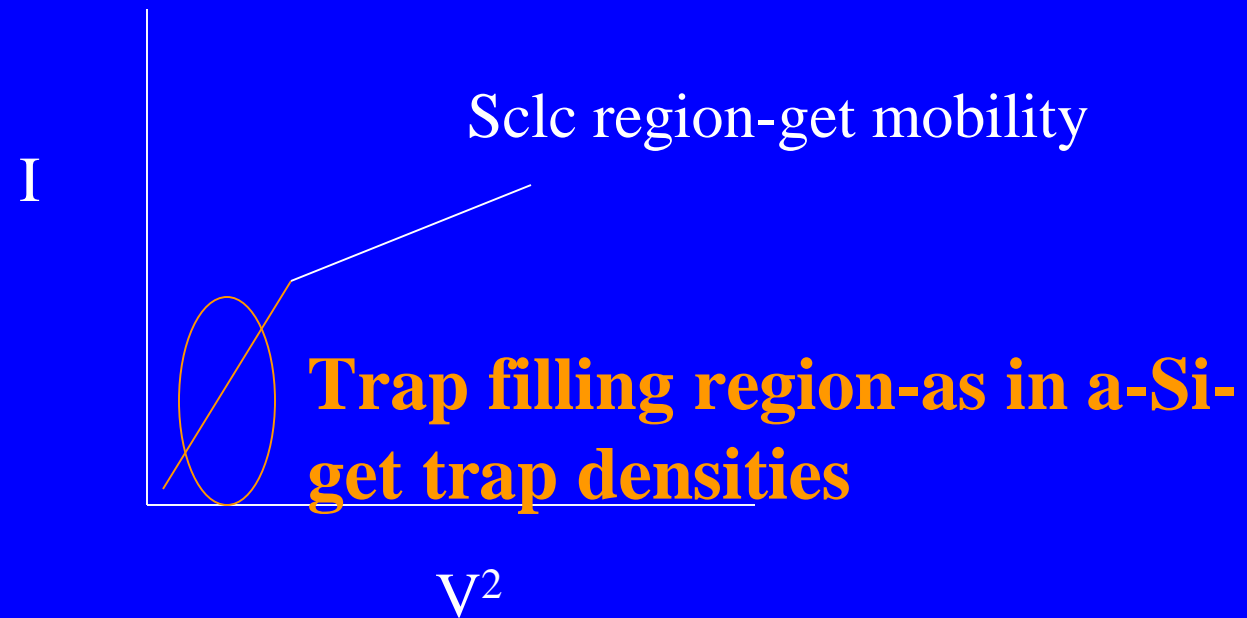


There is always
a transition
layer before
good nc-Si
grows -
minimize this
layer

Lampert model for sclc with single trap



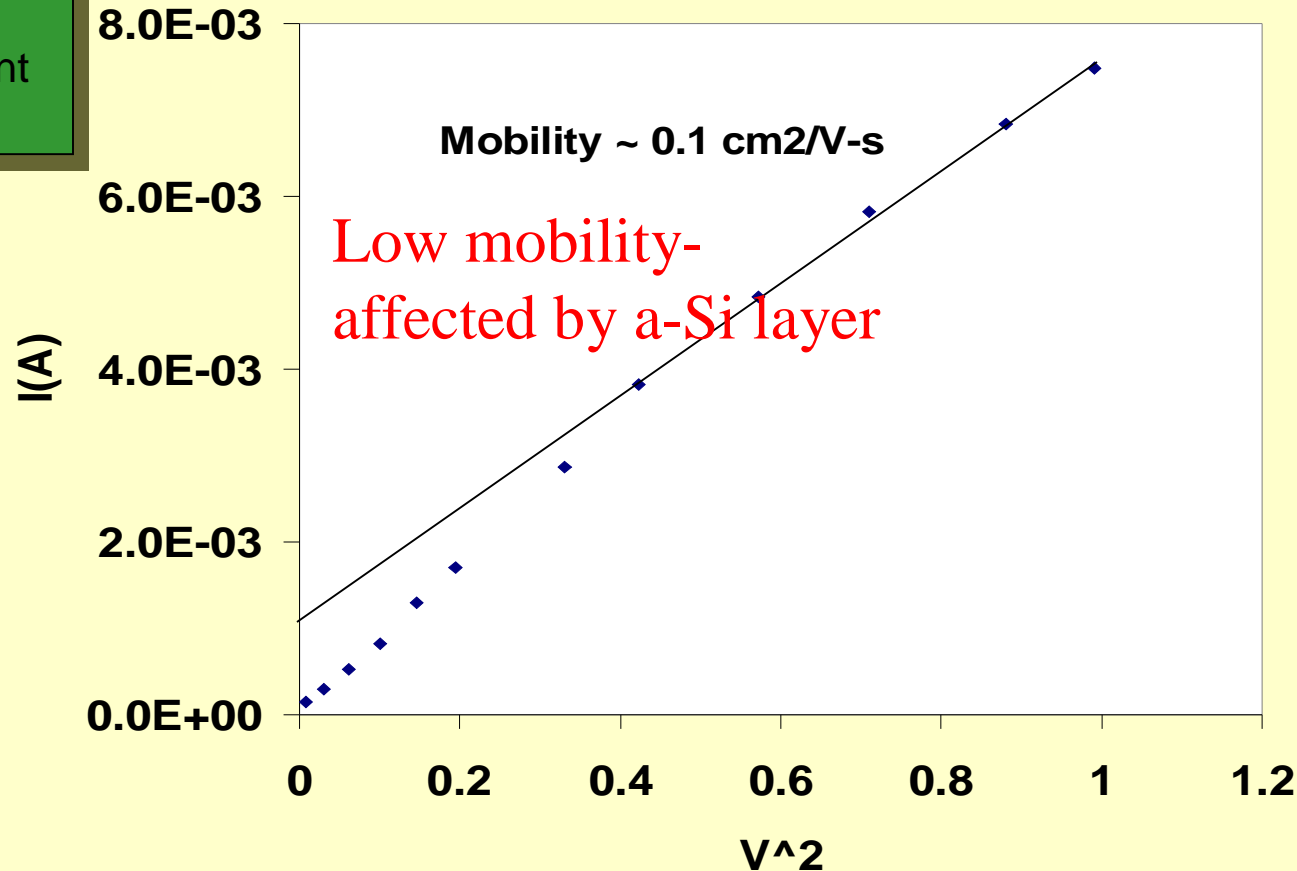
Lampert model :SCLC with Distributed traps



Results when a **thick** transition layer (Did not use high H dilution initially)

Large grain size
(25-30 nm)

But low apparent
mobility



How do we minimize the transition region?

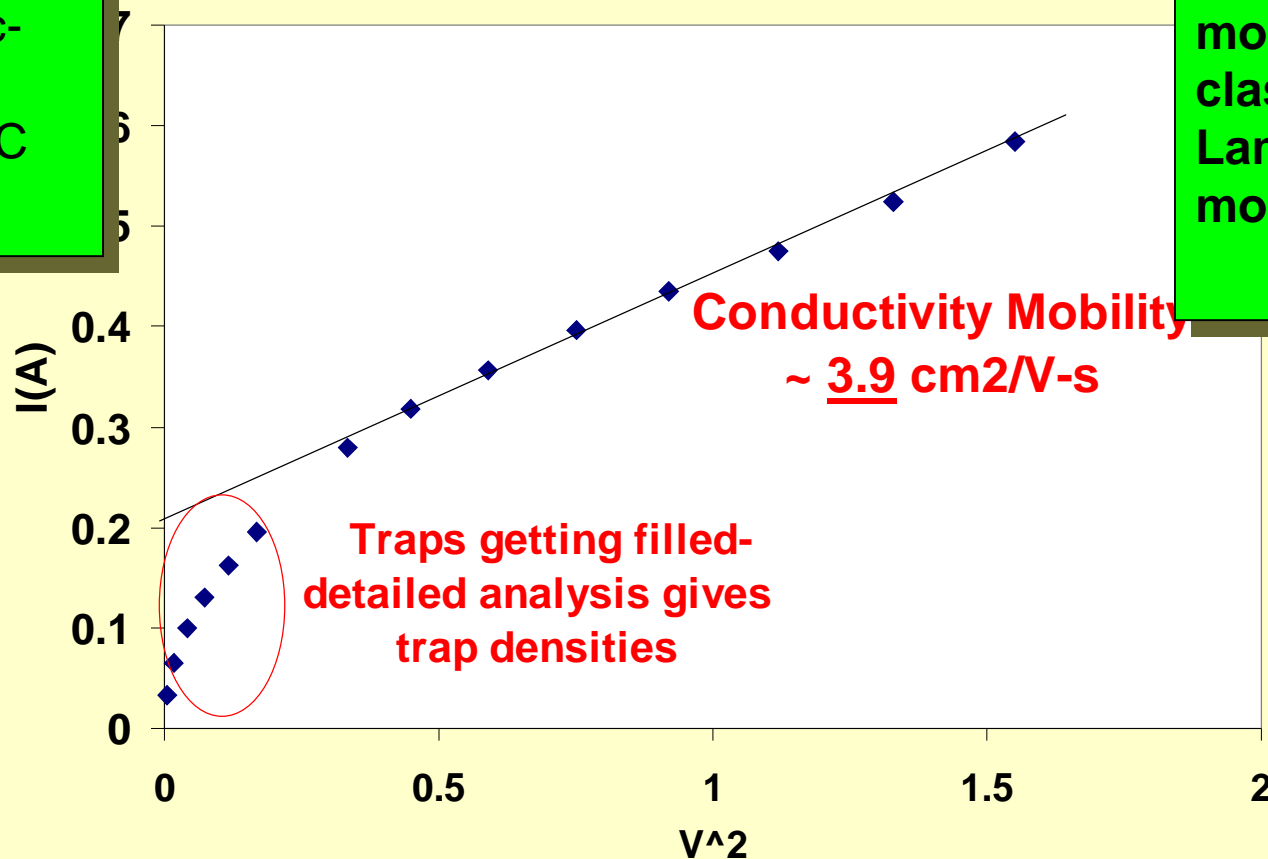
- By using a thin a-Si layer initially (10-20 nm), followed by high H dilution (40:1) conditions, followed by rapidly down-graded H (12:1 ratio)
- Why reduce hydrogen/silane ratio: To get large grains!

Results for nc Si (Hot Wire) with rapid nucleation- grain size (25-30 nm)

3/2004 A3

In nc-Si, traps are limited to about 0.35-0.5 eV below E_c -once full, normal SCLC

Getting reasonable mobilities and classical Lampert-model curves



In the same sample,
measure
simultaneously
defects, diffusion
lengths and mobilities
of both carriers

Conclusions

- SCLC can be used to measure electron mobilities in n^+nn^+
- Diffusion lengths and defects in p^+nn^+
- In principle, we can make n^+ type and p^+ type top contacts on the same samples and measure both hole diffusion lengths and electron mobilities -underway, and hole mobilities with time of flight (Eric?)

Questions for Ken and Bolko

Given that both Eric and I are probably not getting funded, who is going to do the transport and grain enhancement work?

Are larger grains not important?

Is measurement of transport not important?